

Quantum-mechanical description of the chemical bond and the principle of particle identity.

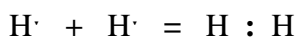
Bezverkhniy Volodymyr Dmytrovych.

Ukraine, e-mail: bezvold@ukr.net

If we consider the physical nature of the chemical bond, then it can be argued that quantum mechanics (the classical approach) describes the chemical bond absolutely formally, that is, in accordance with the aphorism of David Mermin: “Shut up and calculate!”.

Such a formalism is due to the fact that it is not possible to explain the reason for the formation of a chemical bond using the known classical interactions between particles. Since the energy of a chemical bond is a direct consequence of the principle of the identity of particles (in our case, the identity of the bond electrons).

To be more precise, approximately 80 % of the energy of a chemical bond is due precisely to the identity of the bond electrons (in a hydrogen molecule, 5/6 of the bond energy is the exchange energy). Think about the numbers: 80 % of the energy of a chemical bond is energy due to quantum effects!



It should be clearly understood that if there is no identity of electrons (the principle has no analogues in classical mechanics), then there is no reason for the formation of a chemical bond, since using forces in the classical vector form it is impossible to describe a chemical bond.

Let me remind you that the principle of the identity of particles means the fundamental impossibility of experimentally distinguishing identical particles (for example, chemical bond electrons). A consequence of the identity principle is the Pauli principle.

I will especially note that from the above it strictly follows that the “electromagnetic description” of the chemical bond is fundamentally impossible. That is, based only on the Coulomb attraction-repulsion of electrons and nuclei, it is impossible to describe the chemical bond, since the chemical bond has a quantum nature.

Quantum chemistry, for example, the method of molecular orbitals, based precisely on the principle of the identity of particles, provides an approximate mathematical model of molecules. Therefore, in the classical description (used in quantum chemistry), there can be no physical justification for a chemical bond by definition.

Since this question is of fundamental importance for understanding the nature (and problem) of the chemical bond, I will give a few quotes that completely clarify the situation.

“...In addition to electrostatic repulsion between atomic nuclei, in a simple $Y : Y$ molecule there is also repulsion between two electrons that form a bond.

How, in this case, can one generally explain the formation of a bond between individual atoms $Y \cdot$?

It can be argued that the energy necessary for the formation of a bond arises due to the attraction between electrons and nuclei in the following way. The electrons involved in the formation of a bond between two nuclei... are equivalent and indistinguishable. This means that one cannot be considered as belonging to this atom more than to another.

The significance of the pairing of electrons lies in the fact that it gives each of them the greatest possible freedom of movement along the orbitals of a diatomic system, instead of “localization” on individual atoms...

Quantum mechanical calculations indicate that the freedom of movement of electrons is an extremely important factor. This can be seen from the fact that five-sixths of the binding energy in a hydrogen molecule can be attributed to the delocalization of electrons between nuclei...” [1].

Studying organic chemistry in the 3rd year of the university (Department of Chemistry), I used “Fundamentals of Organic Chemistry” (J. Roberts, M. Caserio) as a basic textbook [1]. After reading this quote, I could no longer work, because I understood that there is no physical justification for the chemical bond! My favorite textbook upset me a lot (first and last time). I left the library and walked around the city (Chernivtsi) for a long time, thinking about what it all means...

I would like to emphasize that using only the classical concepts of attraction-repulsion between electrons and nuclei, it is impossible to describe even a one-electron bond, that is, when there is no repulsion between electrons. This was shown in 1928 by L. Pauling using the example of the molecular hydrogen ion (H_2^+).

Pauling analyzed the interaction of a hydrogen atom and a proton over the entire range of lengths (assumed that the hydrogen atom and proton are preserved when approaching), and showed that the bond is not formed in this case [2, 3].

That is, based on classical concepts (Coulomb attraction-repulsion), it is impossible to explain even the formation of a one-electron bond in a molecular hydrogen ion - keep in mind that this system consists of only two protons and one electron $[H \cdot H]^+$.

I will also give an eloquent quote from Louis de Broglie's book “Revolution in Physics”, which briefly and clearly shows the formalism of quantum mechanics in relation to the chemical bond. I studied this book, like many others, when I was trying to find a theoretical justification for a three-electron bond with a multiplicity of 1.5. This book is written very well - the depth of De Broglie's thoughts is simply amazing.

“...Another remarkable application of wave mechanics was the theory of the hydrogen molecule, or more generally, the theory of the homeopolar molecule...

The classical theory to some extent allows us to understand the origin of the bonds connecting the atoms of a heteropolar molecule, that is, a molecule whose atoms have different electron affinities.

Indeed, in this case, one can imagine that the various atoms of the molecule are converted into ions by donating or gaining electrons. Therefore, one can think that the stability of the molecular structure is due to the action of Coulomb forces between the various ions formed.

However, the case of homeopolar molecules, for example, the very important case of molecules consisting of two atoms of the same nature, was previously the most difficult for physicists, since there were no reasons for atoms with the same electron affinity to turn into ions of different signs.

Therefore, it remained unclear what type of forces could act between these neutral atoms to ensure their bonding in the molecule. Everything that came to mind turned out to be too weak for this role.

Wave mechanics makes it possible, and this is no small success, to understand the nature of homeopolar bonds by introducing the concept of exchange energy.

This is what this somewhat mysterious expression means: if we carefully study the behavior of a system containing identical particles using wave mechanics, it turns out that in the expression for the energy of the system, along with terms describing the known interaction between particles, there appear terms of a new type related to the fact that identical particles can change places.

These terms describe what we have called the exchange energy. They correspond to forces of a completely new type, which cannot be represented in the classical vector form and which are huge in magnitude.

These new forces are an inevitable consequence of the formalism of new mechanics, but it turns out that they cannot be explained physically, in the old sense of the word...

Without dwelling any longer on these very interesting properties of exchange energy, we would like to show how to explain the formation of a homeopolar molecule. The simplest example of such a molecule is the hydrogen molecule, which consists of two atoms, each containing one electron. When two hydrogen atoms, initially far apart, begin to approach each other, they tend to form a mechanical system with two electrons. Therefore, an exchange energy appears between these two electrons.

This energy can be calculated by the methods of wave mechanics, taking into account the Pauli principle and the existence of spin. This is what Heitler and London did. They got the following result: if the spin vectors

of both electrons have the same signs, then the exchange energy corresponds to the repulsion between the atoms, and the molecule cannot be formed.

If, on the contrary, the spin vectors have opposite signs, the exchange energy corresponds to the attraction of atoms...

This theory explains well the formation and properties of the hydrogen molecule... the electrons of two hydrogen atoms are able to form a pair with oppositely directed spin vectors. This pair, having a very high stability, is a link between two atoms and forces them to combine into a single molecule...

This shows that the existence of chemical valency is associated with the presence of exchange energy between electrons.

Now it is clear why attempts to explain the valence forces using the vector scheme applicable in other cases did not give a truly satisfactory result.

In addition, the fact that two electrons, forming a pair, are, as it were, neutralized and no longer affect any molecular interactions, explains valence saturation, which is absolutely incompatible with the idea and valences as about forces of the old type...

The Pauli principle expresses a very specific property of electrons and other particles that obey it. Indeed, today it is almost impossible to understand how two identical particles mutually forbid each other to occupy the same state. This type of interaction is completely different from the interaction in classical physics. Its physical nature is still completely unknown to us.

Apparently, this is one of the most important and, moreover, the most difficult tasks that the theoretical physicists of the future will have to solve in order to find out the physical origins of the exclusion principle.

To show how far we have gone from the old ideas, consider the case of a gas of particles of the same nature, obeying the Pauli principle, for example, an electron gas. According to the exclusion principle, no two electrons of this gas can be in the same state of uniform rectilinear motion, because here the states of uniform rectilinear motion are quantized.

From a classical point of view, this would mean that a particle located at some point in a vessel containing a gas would prevent any other gas particle from having the same state. This is completely paradoxical, since a vessel with a gas can be taken as large as desired and, consequently, the distance between particles can be as large as desired. However, this paradox is closely related to the Heisenberg uncertainty relations and disappears if they are taken into account. Indeed, the rectilinear and uniform motion of particles corresponds to a well-defined energy of these particles.

Thus, the uncertainty relations forbid talking about the position and state of motion of two particles at the same time. The very fact that we are talking about the fact that the energy states of the particles are completely determined does not allow us to talk any more about the distance between them, because they are not localized in any way. This example shows that the physical interpretation of the exclusion principle must necessarily be carried out entirely outside the framework of classical concepts...” [4].

In the end, I'll clarify that the formation of chemical bond energy can still be explained physically on the basis of the mass defect of the (relativistic) bond electrons, which makes it possible to accurately predict the range of lengths for “strong” and “weak” chemical bonds based only on the “Bohr radius” of the atom (a chemical bond is a de Broglie standing wave) [5, 6].

This approach also logically leads us to the fact that the electrons of a chemical bond become depersonalized and lose their individuality: after the formation of a bond, individual electrons no longer exist, but there is a “boiling mass” of real electrons and virtual electrons and positrons that are inside the bond.

Indeed, the electrons of a chemical bond are equivalent and literally indistinguishable, which fully corresponds to the principle of identity of identical particles.

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2. Pauling L. Nature of the chemical bond. Translated from English by M. E. Dyatkina under the guidance of professor Y. K. Sirkin, State Scientific and Technical Publishing House of Chemical Literature, Moscow, Leningrad, 1947, p. 25.
3. Pauling, L. (1928). “The Application of the Quantum Mechanics to the Structure of the Hydrogen Molecule and Hydrogen Molecule-Ion and to Related Problems”. Chemical Reviews 5(2): 173–213. Doi: 10.1021/cr60018a003.
4. Louis de Broglie “Revolution in Physics”. P. 125-126, 124. Atomizdat; Moscow; 1965, 134 pages.
5. Bezverkhniy V. D. Bohr Model of the Atom, Mass Defect and Chemical Bond. SSRN Electronic Journal, 5 Dec 2022. <https://dx.doi.org/10.2139/ssrn.4257744>
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